NOVEL ADHESION TEST FOR ENVIRONMENTALLY ASSISTED FRACTURE IN THIN FILMS

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ABSTRACT

Thin films, used in various applications and devices, must strongly adhere to their substrates. Due to various processing and storage environments that devices can be exposed to, water may be introduced into the system. If residual stresses are present in a thin film, delamination propagation can be driven by water without the assistance of an externally applied mechanical force. It is extremely important to measure coating adhesion quantitatively, taking into account environmental effects. This paper describes general mechanics approach to moisture effects on delamination of stressed thin films, with diamond like carbon films (DLC) used in the hard drive industry as an example.

DLC film adhesion has been measured to drop by a factor of 50 to a 100 using the modified superlayer indentation test. Crack propagation rates in DLC films have been recorded up to a few microns per second. The reduction of DLC film adhesion and delamination propagation is attributed to water lowering the surface energy at the crack tip.

Key Words: Adhesion, thin film, environment, sub-critical debonding, fracture.

INTRODUCTION

Thin films and coatings are used everywhere, from car paint to electrical interconnects in a computer processor. There is an endless variety of applications based on the various functional properties of thin films. Many industries, including microelectronics, hard drive, and automotive depend on well-adhered coatings and thin films. For most applications structural performance is also required, for example when corrosion protective coatings [1], wear resistant nitride films on steel [2], surface layers in ceramics [3], and diamond films on titanium [4] are considered.

Coatings and thin films are normally stressed primarily due to the thermal expansion mismatch between the film and the substrate. In case of a flexible substrate, stress in a thin film typically causes

measurable substrate bending. This effect is employed to calculate the macroscopic residual stress in thin films using Stoney's equation [5]. There are many different stress relief mechanisms observed in thin films. The residual stress can be partially relieved by plastic deformation and surface reconstruction [6], or simply by mechanical film failure, especially if the stress levels are high, and, in addition, externally applied mechanical and thermal stresses are present combined with environmental effects. In some cases, films and protective coatings fail due to environmental effects and long-term moisture exposure, causing corrosion of the substrate, or the film, or both.

In addition to corrosion, thin film failures can be also caused by the diffusion of an adhesion-promoting layer over a long period of time, significantly affected by the environmental conditions, temperature, etc. [7]. Here we consider the case when a coating fails to provide corrosion protection due to its adhesion degradation. Coating fracture is very common when the interface is exposed to moist environments. While a coating may pass adhesion tests right after application, it fails the test after certain service time. It is extremely important to measure coating adhesion quantitatively, taking into account environmental effects. In addition to causing corrosion in some cases, especially when metallic substrates are considered, moisture significantly reduces the coating adhesion when it reaches the interface between the coating and the material it is designed to protect.

There are several quantitative adhesion testing techniques available, including the four-point bend test [8], modified lift-off edge test (MELT) [9], and the superlayer indentation test [10, 11] to name a few. This paper describes the environmental effects on thin film delamination, along with the modified version of the superlayer indentation test, capable of assessing adhesion in controlled environments.

ENVIRONMENTALLY-INDUCED FRACTURE

Consider the case when stress in the film and long-term moisture exposure cause its failure. One common example is vintage mirror silver backing degradation (Figure 1a). Everybody is familiar with this sort of failure, but for some reason it has not been sufficiently covered in the literature. Similar effects are seen in larger solar mirrors [12]. Figure 1b presents an image of telephone cord delamination propagation induced by indentation and consequent introduction of water into the delaminating channel formed from a buckled 20 nm diamond-like carbon (DLC) film with a 1 μm W superlayer. Blisters that were not exposed to moisture did not grow [13].

Let's consider the mechanical aspects of thin film delamination process. The strain energy release rate, G, of a stressed film is:

$$G = Z\frac{\sigma^2 h}{E} \qquad (1),$$

where σ is the stress in the film, h is the film thickness, E is its elastic modulus, and Z is a dimensionless cracking parameter. Film will delaminate when the strain energy release rate, G, exceeds the interfacial toughness, $\Gamma_i(\Psi)$:

$$G \geq \Gamma_i(\Psi) \qquad (2).$$

Here, Ψ is the crack phase angle, which is 0° for the mode I, and 90° for the mode II loading. While the amount of energy stored in most stressed solid films is not affected by the moisture presence, the interfacial toughness, $\Gamma_i(\Psi)$ is.

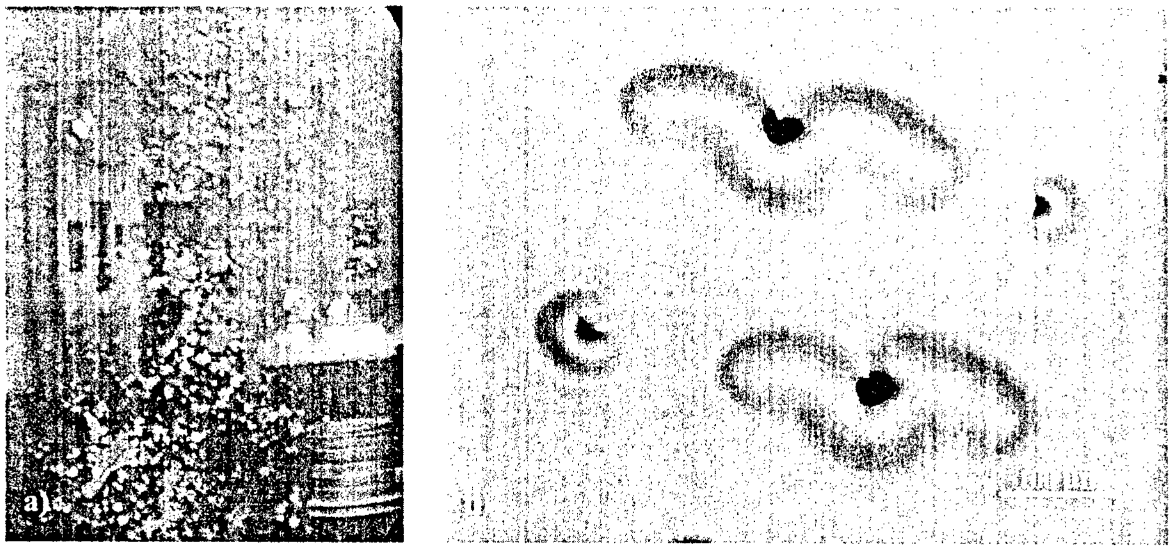

Figure 1. a) Delamination of silver backing on a mirror; b) Telephone cord delamination induced in DCL film by indentation and water.

When a crack propagates along the interface between the film and the substrate, two new surfaces are formed. In the case of brittle fracture with no other energy dissipation mechanisms present, the interfacial toughness would be equal to the sum of the surface energies of the newly formed film and substrate surfaces:

$$\Gamma_i(\Psi) \geq \gamma_{film}^{fracture} + \gamma_{substrate}^{fracture} \quad (3).$$

Even without a chemical reaction present, the moisture would effectively reduce both surface energies. With all variables being equal, the crack propagation rate would reflect the degree of environmental degradation. Table 1 shows the crack propagation rates obtained from a 20 nm DLC film sample in oil, distilled water, as well as in tap water at two test temperatures along with the corresponding Reynolds numbers.

TABLE 1

CRACK PROPAGATION RATES AND REYNOLDS NUMBER OF VARIOUS FLUIDS IN DLC TELEPHONE CORD DELAMINATION CHANNELS.

Fluid Type	Propagation Rate (μm/sec)	Reynolds Number, Re
Oil	0.083	1.3×10^{-8}
Distilled Water	3-5	2.5×10^{-4}
22°C Tap Water	3-5	2.5×10^{-4}
72°C Tap Water	2.5	1.2×10^{-4}

Crack propagation rates are higher in water compared to oil, without noticeable difference between the distilled and the tap water. Raising water temperature to 72 °C slightly decreases the crack propagation rate. It has been previously shown that the film adhesion is increased with temperature due to the reduction of film yield stress, thus larger plastic energy dissipation at the crack tip [11]. Here, similar behavior is observed, where higher film adhesion at higher test temperature results in slower crack propagation rates.

Buckling delamination blisters shown in Figure 1b are useful for studying environmentally assisted fracture. From the buckling profile geometry one can determine the buckling (σ_B) and the residual (σ_r) stresses, as well as $\Gamma_i(\Psi)$ in the direction, perpendicular to the blister propagation [14]:

$$\Gamma_i(\Psi) = \frac{(1-\nu^2)h}{2E}(\sigma_r - \sigma_B)(\sigma_r + 3\sigma_B) \quad (4).$$

Here, E and ν are film's elastic modulus and Poisson's ratio respectively. In the direction of blister propagation, the steady state interfacial toughness, Γ_{SS}

$$\Gamma_{SS} = \frac{(1-\nu^2)h\sigma_r^2}{2E}\left(1 - \frac{\sigma_B}{\sigma_r}\right)^2 \quad (5),$$

is significantly reduced by the moisture presence [13]. We have demonstrated a 100-fold decrease in DLC film adhesion, induced by the moisture presence [15] by means of the modified superlayer indentation test.

MODIFIED SUPERLAYER INDENTATION TEST

In an indentation adhesion test a hard tip (typically made out of diamond) is indented into the film, causing its delamination. The indentation stress, which drives the delamination is then converted into the energy, required to delaminate an area of the film, which is measured optically (Figure 1b). Thus one obtains the practical work of adhesion in terms of the strain energy release rate.

In case of a ductile film on a brittle substrate the film yields, forming plastic pile-up around the indenter instead of delaminating from the substrate. This problem has been addressed by depositing a hard stressed superlayer on top of the film of interest [10]. It prevents coating plastic pile-up upon indentation, and its residual stress provides additional energy for film delamination. Adhesion in terms of the work required to delaminate a unit area of the film is calculated based on the indentation depth and a corresponding delamination blister radius, measured optically (Figure 1b). So far, W, TiW, TaN and TiN films have been used as superlayers.

We have successfully applied the superlayer indentation test to quantitatively measure thin film adhesion in moist environment. Originally conducting the Superlayer indentation adhesion test in water placed over the sample surface showed the same results as in dry laboratory air environment [13]. We modified the test to introduce water at the film interface. For this purpose an introductory indent is first performed to a depth just greater than the film thickness and the tip is unloaded. Water is then introduced, followed by a second indent in the exact same location as the first one in order to further drive crack propagation in moist environment.

Before conducting the double indentation test in water, it was first carried out in a dry environment and compared with the same load single indent test. Test results showed that the strain energy release rate was comparable with the single and double indent tests in a dry environment,

proving the test validity [13]. For the second indent in the double indentation test, the real time load-displacement plot starts from the depth where the introductory indent ended. Since the nanoindenter records the first contact point at zero displacement, the second load-displacement curve was manually shifted to account for this (Figure 2a), allowing to calculate the final indent plastic depth.

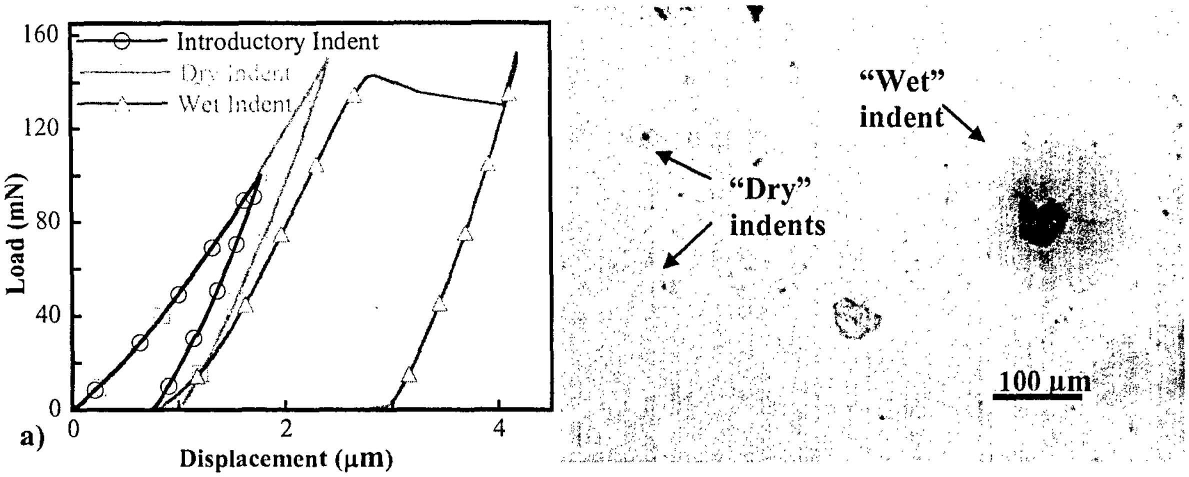

Figure 2. a) Load-displacement curves for indents performed in wet and dry environments; b) Corresponding delamination blisters in wet and dry environments.

The initial indent should be deeper than the film stack thickness test to work, exposing the interface to water. For the indents performed in a wet environment with a deep enough introductory indent and with a second indent to the same maximum load as a single indent in a dry environment, larger delamination blister radius is noticed (Figure 2b). This is attributed to the lower film adhesion in the moist environment. Measurements performed on copper and DLC films showed 50 to 100-fold adhesion degradation [16].

CONCLUSIONS

A novel test for quantifying thin film adhesion in the presence of moisture has been developed based on the superlayer indentation test. DLC films adhesion degradation due to moisture was demonstrated and quantified. Water causes interfacial toughness degradation by reducing the surface energy of the newly formed surfaces. Keeping the interface free of moisture, reducing the film thickness and stress levels would be good ways of failure prevention in the field.

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